PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-166546
(43)Date of publication of application : 24.06.1997

(51)Int.Cl. G01N 21/61
G01N 21/35
G01N 31/00
// G01N 33/483
G01N 33/497

(21)Application number : 08-058052
(22)Date of filing : 14.03.1996

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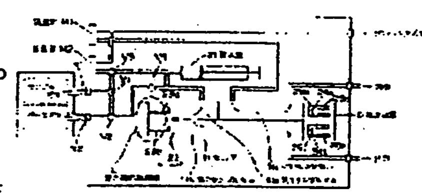
(30)Priority
Priority number : 07263304 Priority date : 11.10.1995 Priority country : JP

(54) ISOTOPE GAS SPECTROMETRY AND ITS DEVICE

(57)Abstract:
PROBLEM TO BE SOLVED: To realize a method, by which in the case of introducing gas to be measured containing plural component gases to a cell to perform spectrometry, the influence of the fluctuation with time of a measurement system can be reduced, and by which the concentration of component gas can be measured precisely.
SOLUTION: A process of filling cells 11a, 11b with reference gas to measure the quantity of light and a process of filling the cells 11a, 11b with gas to be measured to measure the quantity of light are alternately performed. Thus, the absorbance is obtained from of the quantity of light obtained by filling the gas to be measured and the average value of the quantities of light obtained by filling reference gas before and after filling the gas to be measured. At this time, the time fluctuation before and after the measurement of gas to be measured can be corrected by obtaining the average value of quantities of light of reference gas, so that it is possible to remove the influence of the charge with passage of time of a measurement system.



LEGAL STATUS
[Date of request for examination] 14.04.1998
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number] 2885687
[Date of registration] 12.02.1999
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] Lead the measured gas containing two or more component gas to a cel, and it asks for the absorbance of the transmitted light of wavelength suitable for each component gas. In the isotope gas spectrometry approach which measures the concentration of each component gas using the calibration curve created by measuring the measured gas containing the component gas of known concentration The quantity of light of the light obtained by performing by turns the process which fills reference gas in said cel and measures the quantity of light, and the process which **** measured gas in said cel and measures the quantity of light, and filling measured gas, The isotope gas spectrometry approach characterized by calculating an absorbance from the average of the quantity of light of the light obtained by filling the reference gas before and behind that.
[Claim 2] Lead the measured gas containing two or more component gas to a cel, and it asks for the absorbance of the transmitted light of wavelength suitable for each component gas. In the isotope gas spectrometry approach which measures the concentration of each component gas using the calibration curve created by measuring the measured gas containing the component gas of known concentration the process which fills reference gas in said cel and measures the quantity of light, and said cel — him — the process which fills measurement gas and measures the quantity of light being performed by turns, and reference gas with the quantity of light of the light obtained by filling The isotope gas spectrometry approach characterized by calculating an absorbance from the average of the quantity of light of the light obtained by filling the same measured gas before and behind that.
[Claim 3] two or more component gas — carbon-dioxide 12CO2 Carbon-dioxide 13CO2 it is — the isotope gas spectrometry approach according to claim 1 or 2.
[Claim 4] By leading the measured gas containing two or more component gas to a cel, measuring the quantity of light of the transmitted light of wavelength suitable for each component gas, and carrying out data processing of the measured quantity of light with a data-processing means In the isotope gas spectrometry equipment which measures the concentration of component gas said data-processing means An actinometry means to measure the quantity of light of the light corresponding to the wavelength suitable for each component gas by turns about the measured gas and reference gas which were led to the cel, An absorbance calculation means to calculate an absorbance from the average of the quantity of light of the light obtained by filling reference gas, and the quantity of light of the light obtained by filling the measured gas before and behind that, Isotope gas spectrometry equipment characterized by including a concentration calculation means to ask for the concentration of component gas, using the calibration curve created by measuring the measured gas containing the component gas of known concentration.

[Claim 5] By leading the measured gas containing two or more component gas to a cel, measuring the quantity of light of the transmitted light of wavelength suitable for each component gas, and carrying out data processing of the measured quantity of light with a data-processing means In the isotope gas spectrometry equipment which measures the concentration of component gas said data-processing means An actinometry means to measure the quantity of light of the light corresponding to the wavelength suitable for each component gas by turns about the measured gas and reference gas which were led to the cel, An absorbance calculation means to calculate an absorbance from the average of the quantity of light of the light obtained by filling measured gas, and the quantity of light of the light obtained by filling the reference gas before and behind that, Isotope gas spectrometry equipment characterized by including a concentration calculation means to ask for the concentration of component gas, using the calibration curve created by measuring the measured gas containing the component gas of known concentration.

[Claim 6] two or more component gas — carbon-dioxide 12CO2 Carbon-dioxide 13CO2 it is — isotope gas spectrometry equipment according to claim 4 or 5.
[Claim 7] Carbon-dioxide 12CO2 Carbon-dioxide 13CO2 The measured gas included as component gas is led to a cel. In the isotope gas spectrometry approach which measures the concentration of each component gas using the calibration curve created by measuring the gas which asks for the absorbance of the transmitted light of wavelength suitable for each component gas, and contains the component gas of known concentration About two kinds of measured gas collected from one specimen, it is CO2 of one measured gas. Concentration is CO2 of the measured gas of another side. If higher than concentration CO2 of measured gas of one of these Concentration is CO2 of the measured gas of another side. One measured gas is diluted until it becomes equal to concentration, and they are ratio-of-concentration 13CO2 / 12CO2 of each ****** gas. The isotope gas spectrometry approach to measure.
[Claim 8] Carbon-dioxide 12CO2 Carbon-dioxide 13CO2 The measured gas included as component gas is led to a

cel. In the isotope gas spectrometry approach which measures the concentration of each component gas using the calibration curve created by measuring the gas which asks for the absorbance of the transmitted light of wavelength suitable for each component gas, and contains the component gas of known concentration It sets to preliminary measurement and is (a). About two kinds of measured gas collected from one specimen, it is CO2 of the measured gas of the 1st kind. CO2 of concentration and the measured gas of the 2nd kind Measure concentration, respectively and it sets to this measurement. (b) CO2 of the measured measured gas of the 1st kind CO2 of the measured gas by which concentration was measured and whose number is the 2nd If higher than concentration CO2 of this measured gas of the 1st kind CO2 of the measured gas whose concentration is the 2nd kind After diluting the measured gas of the 1st kind until it becomes equal to concentration, Ratio-of-concentration 13CO2 / 12CO2 of the measured gas of the 1st kind It measures and is (c). Ratio-of-concentration 13CO2 / 12CO2 of the measured gas of the 2nd kind The isotope gas spectrometry approach to measure.
[Claim 9] Carbon-dioxide 12CO2 Carbon-dioxide 13CO2 The measured gas included as component gas is led to a cel. In the isotope gas spectrometry approach which measures the concentration of each component gas using the calibration curve created by measuring the gas which asks for the absorbance of the transmitted light of wavelength suitable for each component gas, and contains the component gas of known concentration It sets to preliminary measurement and is (a). About two kinds of measured gas collected from one specimen, it is CO2 of the measured gas of the 1st kind. CO2 of concentration and the measured gas of the 2nd kind Measure concentration, respectively and it sets to this measurement. (b) CO2 of the measured measured gas of the 1st kind CO2 of the measured gas by which concentration was measured and whose number is the 2nd If lower than concentration Ratio-of-concentration 13CO2 / 12CO2 of the measured gas of the 1st kind It measures as it is. (c) CO2 of the measured gas of the 2nd kind CO2 of the measured gas whose concentration is the 1st kind Ratio-of-concentration 13CO2 / 12CO2 of the measured gas of the 2nd kind after diluting the measured gas of the 2nd kind until it becomes equal to concentration The isotope gas spectrometry approach to measure.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Since a living body's metabolism can be measured by measuring concentration change of an isotope, or change of the ratio of concentration after medicating a living body with the drug containing an isotope, analysis of an isotope is used for the sick diagnosis in the field of medical. Moreover, also except the medical field, analysis of an isotope is used for research of photosynthesis, and research of vegetable metabolism, and is used for trace of an ecosystem in the geochemistry field.
[0002] This invention relates to the isotope gas spectrometry approach and measuring device which measure the concentration of isotope gas paying attention to a difference of the light absorption property of an isotope.
[0003]
[Description of the Prior Art] It is known that the bacteria called HERIKOBAKUTAPIRORI (H.P.) other than stress generally exist as a cause of a gastric ulcer and gastritis. If HP exists in a patient's stomach, it is necessary to perform the disinfection therapy by administration of an antibiotic etc. Therefore, it is important to check whether HP exists in a patient. HP has strong urease activity and disassembles a urea into a carbon dioxide and ammonia.
[0004] On the other hand, although the mass number exists [the thing of 12 etc.] and the isotope of 13 or 14 exists [the mass number] in carbon, since isotope 13C of 13 does not have radioactivity and the mass number stabilizes and exists in these, handling is easy. Then, 13COs2 in the exhalation of the patient who is the last metabolite after medicating a living body with the urea which carried out marking by isotope 13C In concentration and a concrete target, they are 13COs2. 12COs2 Existence of HP can be checked if the ratio of concentration can be measured.
[0005] However, 13CO2 12COs2 The ratio of concentration is as large as 1:100, and difficult for measuring the ratio of concentration in a patient's exhalation with a sufficient precision for this reason in a nature. The former and 13CO2 12COs2 The approach using infrared spectroscopy as an approach of asking for the ratio of concentration is learned (refer to JP,61-42219,B and JP,61-42220,B).
[0006] An approach given in JP,61-42220,B prepares the cel of two merits and demerits, and is 13COs2 in one cel. 12COs2 in absorption and one cel It is the approach of measuring the optical reinforcement in the wavelength which makes it the die length of a cel to which absorption becomes equal, leads the light which penetrated two cels to both cels, and realizes optimum sensitivity, respectively. If according to this approach the light absorption ratio in the ratio of concentration of a nature can be set to 1 and the ratio of concentration shifts after this, since a light absorption ratio shifts, only the part shifted can know change of a light absorption ratio, and change of the ratio of concentration can be known.
[0007]
[Problem(s) to be Solved by the Invention] CO2 Concentration, especially 13COs2 Since concentration is very thin, high sensitivity must be measured. However, if there is fluctuation of many constants of system of measurement, such as fluctuation of the reinforcement of the light source, temperature fluctuation of gas itself, temperature fluctuation of the cel which introduces gas, and fluctuation of the sensibility of photodetection equipment, when the sensibility of measurement is raised, the measured quantity of light also reacts sensitively and has the problem that an error arises in measured value by factors other than actual measured gas.
[0008] Although it is possible to start measurement after spending many hours enough until system of measurement falls and sticks in order to solve the aforementioned problem, if it carries out like this, a throughput will decline, and it becomes impossible to respond to a user's request of wanting to measure a lot of samples for a short time. Moreover, it sets to measurement and is 12CO2 about one kind of exhalation. An absorbance is measured and it is 12CO2. The calibration curve of ** is used and they are 12COs2. Concentration is computed and it is 13CO2. An absorbance is measured and it is 13CO2. The calibration curve of ** is used and they are 13COs2. Concentration is computed. Measurement with the same said of the exhalation of other classes is carried out.
[0009] At this time, it is CO2. If concentration is almost the same about the exhalation whose number is two, it is 12CO2. A calibration curve and 13COs2 The range using a calibration curve can be narrowed. Therefore, the accuracy of measurement can be raised by limiting the range using a calibration curve. Then, when solving an above-mentioned technical technical problem, leading the measured gas containing two or more component gas to a cel and carrying out spectrometry, this invention can reduce the effect of the time variation of system of measurement, and aims at realizing the isotope gas spectrometry approach and measuring device which can measure the concentration of component gas to a precision.

[0010] Moreover, this invention aims at realizing the isotope gas spectrometry approach which can measure the concentration of component gas to a precision by limiting the range using a calibration curve, when leading the measured gas containing two or more component gas to a cel and carrying out spectrometry.
[0011]
[Means for Solving the Problem] The isotope gas spectrometry approach according to claim 1 for attaining the aforementioned purpose is an approach of calculating an absorbance from the average of the quantity of light of the light obtained by performing by turns the process which fills reference gas in a cel and measures the quantity of light, and the process which fills measured gas in said cel and measures the quantity of light, and filling measured gas, and the quantity of light of the light obtained by filling the reference gas before and behind that.
[0012] Measurement of an absorbance performs the process which fills reference gas and measures the quantity of light, and the process which fills measured gas in said cel and measures the quantity of light by a unit of 1 time, and although it usually asks for an absorbance, according to the approach of this invention, it is calculating the absorbance from the average of the quantity of light of the light obtained by filling measured gas, and the quantity of light of the light obtained by filling the reference gas before and behind that.
[0013] By this, a part for the time variation before and behind measured gas determination can be amended by taking the average of the quantity of light of reference gas, and the effect of aging of system of measurement can be removed. In addition, since the measurement result of the reference gas after measurement of measured gas also brings a measurement result of reference gas before measurement of the following measured gas, the measurement result of 1 time of reference gas is utilizable for a duplex.
[0014] Moreover, an absorbance is calculated from the average of the quantity of light of the light obtained by filling reference gas with the isotope gas spectrometry approach according to claim 2, and the quantity of light of the light obtained by filling the same measured gas before and behind that. By this approach, since the same measured gas must be measured twice, although effectiveness falls, also by this approach, it can amend a part for the time variation before and behind measured gas determination by taking the average of the quantity of light of measured gas, and can remove the effect of aging of system of measurement.
[0015] Moreover, isotope gas spectrometry equipment according to claim 4 is applied to the same invention as the isotope gas spectrometry approach according to claim 1, and isotope gas spectrometry equipment according to claim 5 is applied to the same invention as the isotope gas spectrometry approach according to claim 2. two or more component gas — carbon-dioxide $^{12}CO_2$ Carbon-dioxide $^{13}CO_2$ you may be (claims 3 and 6) .
[0016] Moreover, the isotope gas spectrometry approach according to claim 7 About two kinds of measured gas collected from one specimen, it is CO_2 of one measured gas. Concentration is CO_2 of the measured gas of another side. If higher than concentration CO_2 of measured gas of one of these Concentration is CO_2 of the measured gas of another side. One measured gas is diluted until it becomes equal to concentration, and they are ratio-of-concentration $^{13}CO_2$ / $^{12}CO_2$ of each ****** gas. It is the approach of measuring.
[0017] According to this approach, it is CO_2. On the conditions that concentration is equal, since two kinds of exhalation can be measured, respectively, the range of the calibration curve to be used can be limited. Consequently, the accuracy of measurement can be raised. Each approach according to claim 8 or 9 fills the measured gas of the 1st kind in a single cel, and after it measures and discharges the quantity of light, it shows the concrete procedure of the isotope gas spectrometry approach according to claim 7 on condition of filling the measured gas of the 2nd kind and measuring the quantity of light.
[0018]
[Embodiment of the Invention] 13COs2 in exhalation after medicating human being with the urea diagnostic drug which carried out marking by isotope 13C hereafter The gestalt of the operation of this invention in the case of carrying out the spectrometry of the concentration is explained to a detail, referring to an accompanying drawing.
I. The exhalation of the patient before prescribing exhalation test **** and an urea diagnostic drug for the patient is collected in an exhalation bag. The capacity of an exhalation bag is good at about 250ml. Then, an urea diagnostic drug is administered orally and exhalation is collected in an exhalation bag by the same approach after 10 to 15 minutes, and as administration before.
[0019] The exhalation bag after prescribing a medicine for the patient before administration is set to the predetermined nozzle of isotope gas spectrometry equipment, respectively, and the following automatic control is performed.
II. isotope gas spectrometry equipment drawing 1 is the block diagram showing the whole isotope gas spectrometry equipment configuration. The exhalation bag which collected the exhalation after administration (henceforth "sample gas"), and the exhalation bag which collected the exhalation before administration (henceforth "gase gas") are a nozzle N1 and N2, respectively. It is set. Nozzle N1 It lets a transparence resin pipe (only henceforth a "pipe") pass, and is V1 to the Mikata bulb. It is connected and is a nozzle N2. It lets a pipe pass and is the Mikata bulb V2. It is connected.
[0020] On the other hand, it is reference gas (if it is gas which does not have absorption in a measuring object wavelength region, it is good anything.) from a chemical cylinder. For example, nitrogen gas is supplied. Reference gas is divided into a two way type, and one side is a flowmeter M1. It lets it pass, and goes into reference cell 11c, and another side is a flowmeter M2. It lets it pass and is the Mikata bulb V3. It leads. The reference gas included in reference cell 11c comes out of reference cell 11c, and is discharged as it is.
[0021] Mikata bulb V3 from — it was divided — on the other hand, Mikata bulb V1 being connected — another side — $^{12}CO_2$ It is connected with 1st sample cel 11a for measuring absorption. moreover, Mikata bulb V2 from — it

was divided — on the other hand, two-way-type bulb V4 letting it pass — 1st sample cel 11a — being connected -- another side — Mikata bulb V1 It is connected. Furthermore, Mikata HARUBU V3 Between 1st sample cel 11a, it intervenes in the insufflation machine 21 (capacity of 60 cc) for pouring in sample gas or gase gas quantitatively. This insufflation machine 21 is the thing of a configuration like a syringe which has a piston and a cylinder, and the drive of a piston is performed by having two incomes with the motor which is not illustrated, the delivery screw connected with the motor, and the nut fixed to the piston.

[0022] The cel room 11 is 12CO2, as shown in drawing 1 . Short 1st sample cel 11a for measuring absorption, 13COs2 It consists of reference cell 11c which passes long 2nd sample cel 11b for measuring absorption, and reference gas. 1st sample cel 11a and 2nd sample cel 11b are open for free passage, and the gas led to 1st sample cel 11a goes into 2nd sample cel 11b as it is, and is exhausted. Moreover, reference gas is drawn and exhausted by reference cell 11c. The die length of 1st sample cel 11a is specifically 13mm, the die length of 2nd sample cel 11b is specifically 250mm, and the die length of reference cell 11c is specifically 236mm.

[0023] Sign L shows infrared light equipment. Infrared light equipment L is equipped with two waveguides 23a and 23b for irradiating infrared radiation. The method of infrared generating is easy to be the thing of arbitration, for example, its ceramic heater (skin temperature of 450 degrees C) etc. is usable. Moreover, the rotating chopper 22 which infrared radiation is broken [chopper] a fixed period and passes it is formed. The optical path which what passes along 1st sample cel 11a and reference cell 11c among the infrared radiation irradiated from infrared light equipment L forms is called "1st optical path", and the optical path which what passes along 2nd sample cel 11b forms is called "2nd optical path" (refer to drawing 2).

[0024] Sign D shows the infrared detection equipment which detects the infrared radiation which passed the cel. Infrared detection equipment D is equipped with 1st wavelength filter 24a put on the 1st optical path, the 1st sensing element 25a, 2nd wavelength filter 24b put on the 2nd optical path, and 2nd sensing element 25b. 1st wavelength filter 24a is 12CO2. In order to measure absorption, through (bandwidth of about 20nm) and 2nd wavelength filter 24b are 13CO2 about infrared radiation with a wavelength of about 4280nm. In order to measure absorption, it is designed so that it may let infrared radiation with a wavelength of about 4412nm pass (bandwidth of about 50nm). If the 1st sensing element 25a and 2nd sensing element 25b are components which detect infrared radiation, they are easy to be the thing of arbitration, for example, a semi-conductor infrared sensor called PbSe is used.

[0025] 1st wavelength filter 24a and 1st sensing element 25a are contained into package 26a filled with inert gas, such as Ar, and contained in package 26b by which 2nd wavelength filter 24b and 2nd sensing element 25b were similarly filled with inert gas. The whole infrared detection equipment D is maintained at constant temperature (25-degreeC) by a heater and the Peltier device, and the part of the sensing element in Packages 26a and 26b is maintained at 0-degreeC by the Peltier device.

[0026] Drawing 2 is the sectional view showing the detailed structure of said cel room 11. the cel room 11 is a product made from stainless steel in itself, and four directions should be caught with a metal plate (for example, brass plate) 12 — it is sealed with the heat insulator 14 through the heater 13 installed in the upper and lower sides or right and left. It is divided into two steps, 1st sample cel 11a and reference cell 11c are arranged in one stage, and 2nd sample cel 11b is arranged in the stage of another side by the inside of the cel room 11.

[0027] The 1st optical path passes in a serial at 1st sample cel 11a and reference cell 11c, and the 2nd optical path passes in 2nd sample cel 11b. Signs 15, 16, and 17 are sapphire transparency apertures which make infrared radiation penetrate. Said cel room 11 is controlled so that it is maintained at constant temperature (40 degrees C) by the heater 13.

IIIa. measurement-procedure 1 measurement — reference gas determination -> gase gas — the procedure measurement -> reference gas determination -> sample gas determination -> reference gas determination ->.... performs. However, besides this procedure, although gase gas measurement -> reference gas determination -> gase gas measurement, sample gas determination -> reference gas determination -> sample gas determination, and the procedure .... may be used, since the same gase gas and sample gas must be measured twice, effectiveness falls. Hereafter, the procedure of the efficient former is explained.

[0028] To reference cell 11c, reference gas is always flowing during measurement.

As shown in IIIa-1. reference measurement drawing 3 , 200ml/m of pure reference gas is passed in the gas passageway and the cel room 11 of isotope gas spectrometry equipment for about 15 seconds, and washing of a gas passageway and the cel room 11 is carried out to them.

[0029] Next, as shown in drawing 4 , a gas passageway is changed and washing of a sink, a gas passageway, and the cel room 11 is carried out for reference gas. Actinometry is carried out by each sensing element 25a and 25b after about 30-second progress. Thus, reference measurement is carried out for computing an absorbance. Thus, it is the quantity of light obtained by 12R1 and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a 13R1 It writes.

As IIIa-2. gase gas measurement, next reference gas do not flow 1st sample cel 11a and 2nd sample cel 11b, they inhale gase gas with the insufflation vessel 21 from an exhalation bag (refer to drawing 5).

[0030] After inhaling gase gas, as shown in drawing 6 , gase gas is mechanically extruded with constant flow using the insufflation machine 21. In the meantime, actinometry is carried out by each sensing element 25a and 25b. Thus, the quantity of light obtained by 12B and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a is written to be 13B.

Washing of IIIa-3. reference measurement re-**, a gas passageway, and a cel and actinometry of reference gas are

carried out (refer to drawing 3 and drawing 4).
[0031] Thus, the quantity of light 12R2 obtained by 1st sensing element 25a and the quantity of light 13R2 obtained by 2nd sensing element 25b It writes.
As IIIa-4. sample gas determination reference gas does not flow 1st sample cel 11a and 2nd sample cel 11b, it inhales sample gas with the insufflation vessel 21 from an exhalation bag (refer to drawing 7).
[0032] After inhaling sample gas, as shown in drawing 8 , sample gas is mechanically extruded with constant speed using the insufflation machine 21. In the meantime, actinometry is carried out by each sensing element 25a and 25b. Thus, the quantity of light obtained by 12S and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a is written to be 13S.
Washing of IIIa-5. reference measurement re-**, a gas passageway, and a cel and actinometry of reference gas are carried out (refer to drawing 3 and drawing 4).
[0033] Thus, it is the quantity of light obtained by 12R3 and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a 13R3 It writes.
At the IIIb. measurement-procedure 2 aforementioned measurement procedure 1, it is CO2 of gase gas. CO2 of concentration and sample gas It had not carried out making concentration in agreement.
[0034] However, CO2 If concentration is the same about gase gas and sample gas, it is 12CO2. A calibration curve and 13COs2 The range using a calibration curve can be narrowed. Therefore, the accuracy of measurement can be raised by limiting the range using a calibration curve. At this measurement procedure 2, it is CO2 of gase gas. CO2 of concentration and sample gas In order to make concentration mostly in agreement, It sets to preliminary measurement first and is CO2 of gase gas. Concentration and CO2 of sample gas Measure concentration, respectively and it sets to this measurement. CO2 of the gase gas by which preliminary measurement was carried out CO2 of the sample gas by which preliminary measurement of the concentration was carried out If higher than concentration CO2 of this gase gas Concentration is CO2 of sample gas. After diluting gase gas until it becomes equal to concentration, the concentration of gase gas is measured and the concentration of sample gas is measured after that.
[0035] CO2 of the gase gas by which preliminary measurement was carried out in this measurement CO2 of the sample gas by which preliminary measurement of the concentration was carried out If lower than concentration, the concentration of gase gas will be measured as it is, and it is CO2 of sample gas. Concentration is CO2 of gase gas. CO2 of sample gas after diluting sample gas until it becomes equal to concentration Concentration is measured. measurement — gase gas preliminary measurement -> sample gas preliminary measurement -> reference gas determination -> gase gas — the procedure measurement -> reference gas determination -> sample gas determination -> reference gas determination ->.... performs.
While passing pure reference gas in the gas passageway and the cel room 11 of IIIb-1. gase gas preliminary measurement isotope gas spectrometry equipment and carrying out washing of a gas passageway and the cel room 11 to them, the reference quantity of light is measured.
[0036] Next, from an exhalation bag, gase gas is inhaled with the insufflation vessel 21, and gase gas is mechanically extruded with constant flow using the insufflation machine 21. Actinometry of gase gas is carried out by sensing element 25a in the meantime, a calibration curve is used with the absorbance, and it is CO2. It asks for concentration.
While passing pure reference gas in the gas passageway and the cel room 11 of IIIb-2. sample gas preliminary measurement isotope gas spectrometry equipment and carrying out washing of a gas passageway and the cel room 11 to them, the reference quantity of light is measured.
[0037] Next, from an exhalation bag, sample gas is inhaled with the insufflation vessel 21, and sample gas is mechanically extruded with constant speed using the insufflation machine 21. Actinometry of sample gas is carried out by sensing element 25a in the meantime, a calibration curve is used with the absorbance, and it is CO2. It asks for concentration.
IIIb-3. reference measurement, next a gas passageway are changed, and washing of a sink, a gas passageway, and the cel room 11 is carried out for reference gas. Actinometry is carried out by each sensing element 25a and 25b after about 30-second progress.
[0038] Thus, it is the quantity of light obtained by 12R1 and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a 13R1 It writes.
CO2 of the gase gas obtained by 1st sensing element 25a in IIIb-4. gase gas measurement "IIIb-1. gase gas preliminary measurement" Concentration, CO2 of the sample gas obtained by 1st sensing element 25a in "IIIb-2. sample gas preliminary measurement" Concentration is measured. CO2 of gase gas Concentration is CO2 of sample gas. When deeper than concentration, it is CO2 of gase gas in the insufflation machine 21. CO2 of concentration and sample gas After diluting gase gas with reference gas until concentration becomes an equal rate, actinometry of gase gas is carried out.
[0039] Thus, since it dilutes, it is CO2 about two kinds of exhalation. Since concentration can be made almost the same, it is 12CO2. A calibration curve and 13COs2 The range using a calibration curve can be narrowed. In addition, at the measurement procedure 2 of this operation gestalt, it is CO2 about two kinds of exhalation. CO2 which the place which makes concentration almost the same has a meaning, and is indicated by JP,4-12414,B It should be cautious of it not being necessary to necessarily adopt the procedure which always keeps concentration constant. CO2 of gase gas and sample gas It is because the purpose of narrowing the range using a calibration curve can be enough attained if concentration can be made the same. According to actual measurement, it is CO2 of gase gas or

sample gas. Since there are 1 to 5% and variation, concentration is CO2. Always keeping concentration constant requires time and effort very much.

[0040] It is CO2 of gase gas. Concentration is CO2 of sample gas. When thinner than concentration, this gase gas is measured as it is without diluting gase gas. Measurement extrudes gase gas mechanically with constant flow using the insufflation machine 21, and each sensing element 25a and 25b performs it in the meantime. Thus, the quantity of light obtained by 12B and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a is written to be 13B.

Washing of IIIb-5. reference measurement re-**, a gas passageway, and a cel and actinometry of reference gas are carried out.

[0041] Thus, the quantity of light 12R2 obtained by 1st sensing element 25a and the quantity of light 13R2 obtained by 2nd sensing element 25b It writes.

When gase gas is diluted with IIIb-6. sample gas determination "IIIb-4. gase gas measurement", after inhaling sample gas from an exhalation bag, sample gas is mechanically extruded with constant flow using the insufflation machine 21, and actinometry is carried out by each sensing element 25a and 25b in the meantime.

[0042] When gase gas is not diluted with "IIIb-4. gase gas measurement", it is CO2 of sample gas in the insufflation machine 21. CO2 of concentration and gase gas After diluting sample gas with reference gas until concentration becomes an equal rate, actinometry of sample gas is carried out by each sensing element 25a and 25b. Thus, the quantity of light obtained by 12S and 2nd sensing element 25b in the quantity of light obtained by 1st sensing element 25a is written to be 13S.

Washing of IIIb-7. reference gas determination re-**, a gas passageway, and a cel and actinometry of reference gas are carried out.

[0043] Thus, the quantity of light 12R3 obtained by 1st sensing element 25a and the quantity of light 13R3 obtained by 2nd sensing element 25b It writes.

The amount 12R1 of transmitted lights of the reference gas obtained by calculation ****, said measurement procedure 1, or measurement procedure 2 of an absorbance of IV. data-processing IV-1. gase gas, 13R1, the amounts 12B and 13B of transmitted lights of gase gas, the amount 12R2 of transmitted lights of reference gas, and 13R2 12COs [in / it uses and / gase gas]2 Absorbance 12Abs(B) 13CO2 Absorbance 13Abs(B) It asks.

[0044] It is here and they are 12COs2. Absorbance 12Abs(B) 12Abs(B) =-log [212B/(12R1+12R2)]

It comes out and asks and is 13CO2. Absorbance 13Abs(B) 13Abs(B) =-log [213B/(13R1+13R2)]

It comes out and asks.

[0045] Thus, since the average value (R1+R2)/2 of the quantity of light of the reference measurement performed in order are taken and the absorbance is computed using the average value and the quantity of light obtained by gase gas measurement when computing an absorbance, it is a drift (time amount change should affect measurement). Effect can be offset. Therefore, it is until it becomes thermal equilibrium completely at the time of starting of equipment (it usually takes several hours). Even if it does not wait, measurement can be begun promptly.

[0046] In addition, when the glue-stock-SUGASU measurement -> reference gas determination -> gase gas measurement -> sample gas determination -> reference gas determination -> sample gas determination and .... procedure in which the beginning of IIIa. described is adopted, they are 12COs2 of gase gas. Absorbance 12Abs(B) is 12Abs(B). =-log [(12B1+12 B-2) /212R]

It comes out and asks and is 13CO2. Absorbance 13Abs(B) 13Abs(B) =-log [(13B1+13 B-2) /213R]

It comes out and asks. Here, R is the amount of transmitted lights of reference gas, B1, and B-2. It is the amount of transmitted lights of the gase gas before and behind measurement of reference gas, respectively.

IV-2. The amount 12R2 of transmitted lights of the reference gas obtained by the calculation next said measurement procedure 1, or measurement procedure 2 of an absorbance of sample gas, 13R2, the amounts 12S and 13S of transmitted lights of sample gas, the amount 12R3 of transmitted lights of reference gas, and 13R3 12COs [in / it uses and / sample gas]2 Absorbance 12Abs(S) 13CO2 Absorbance 13Abs(S) It asks.

[0047] It is here and they are 12COs2. Absorbance 12Abs(S) 12Abs(S) =-log [212S/(12R2+12R3)]

It comes out and asks and is 13CO2. Absorbance 13Abs(S) 13Abs(S) =-log [213S (13R2+13R3)]

It comes out and asks.

[0048] Thus, since the quantity of light average of the reference measurement performed in order is taken and the absorbance is computed using the average and the quantity of light obtained by sample gas determination when computing an absorbance, the effect of a drift can be offset. In addition, when the glue-stock-SUGASU measurement -> reference gas determination -> gase gas measurement, sample gas determination -> reference gas determination -> sample gas determination, and .... procedure in which the beginning of IIIa. described is adopted, they are 12COs2 of sample gas. Absorbance 12Abs(S) 12Abs(S) =-log [(12S1+12S2) /212R]

It comes out and asks and is 13CO2. Absorbance 13Abs(S) 13Abs(S) =-log [(13S1+13S2) /213R]

It comes out and asks. Here, R is the amount of transmitted lights of reference gas, S1, and S2. It is the amount of transmitted lights of the sample gas before and behind measurement of reference gas, respectively.

The calculation calibration curve of IV-3. concentration is used, and it is 12CO2. Concentration and 13COs2 It asks for concentration.

[0049] A calibration curve is 12CO2. The measured gas which concentration understands, and 13CO2 It creates using the measured gas which concentration understands. In order to search for a calibration curve, it is 12CO2. Concentration is changed in 0% - about 6% of range, and it is 13CO2. An absorbance is measured. They are 12COs2 about an axis of abscissa. For concentration, they are 12COs2 about an axis of ordinate. For an absorbance, it plots

and a curve is determined using a least square method. Since what was approximated by the secondary formula became a curve with comparatively few errors, it has adopted the calibration curve approximated by the secondary formula with this operation gestalt.
[0050] Moreover, 13CO2 Concentration is changed in 0.00% - about 0.07% of range, and it is 13CO2. An absorbance is measured. They are 13COs2 about an axis of abscissa. For concentration, they are 13COs2 about an axis of ordinate. For an absorbance, it plots and a curve is determined using a least square method. Since what was approximated by the secondary formula became a curve with comparatively few errors, it has adopted the calibration curve approximated by the secondary formula with this operation gestalt.
[0051] In addition, when it says strictly, it is 12CO2. Close is [the gas which is, and] 13CO2. Close is [measuring the gas which is independently, respectively, and] 12CO2. 13COs2 By measuring the gas currently mixed, it is 13CO2. An absorbance is different. This is [that the wavelength filter to be used has a bandwidth and] 12CO2. An absorption spectrum and 13COs2 It is because a part of absorption spectrum has lapped. By this measurement, it is 12CO2. 13COs2 Since the gas currently mixed is made into the measuring object, when determining a calibration curve, it is necessary to amend a part for said lap. In this measurement, the calibration curve of an absorption spectrum which amended the lap in part is actually adopted.
[0052] 12COs2 in gase gas calculated using said calibration curve concentration — 12Conc(s) (B) 13COs2 in gase gas concentration — 13Conc(s) (B) 12COs2 in sample gas concentration — 12Conc(s) (S) 13COs2 in sample gas concentration — 13Conc(s) (S) ** — it writes.
Calculation 13CO2 of the IV-4. ratio of concentration 12COs2 It asks for the ratio of concentration. The ratio of concentration in gase gas is 13Conc (B). The ratio of concentration in /12Conc(B) sample gas is 13Conc (S). It asks by /12Conc (S).
[0053] In addition, the ratio of concentration is 13Conc (B). /12Conc(B)+13Conc (B), and 13Conc(S) / 12Conc (S) +13Conc (S) A definition may be given. 12COs2 The ways of concentration are 13COs2. It is because it is farther [than concentration] large, so all serve as the almost same value.
A changed part of 13C which compared changed the decision sample gas and gase gas of IV-5.13C is called for by the following formula.
[0054] delta13C= [ratio of concentration of ratio-of-concentration-gase gas of sample gas] x103/[the ratio of concentration of gase gas] (unit: per mille (permillage)) [0055]
[Example] They are 12COs2 by this isotope gas spectrometry equipment to the same measured gas (naturally the concentration of CO2 is also the same) containing carbon dioxide gas. Multiple-times measurement of the concentration was carried out. 1 hour after equipment starting and a reference gas determination -> sample — the procedure gas determination -> reference gas determination -> sample gas determination -> reference gas determination ->.... performed sample gas determination 10 times. It asked for concentration, respectively by the approach A of this invention of asking for the absorbance of sample gas based on the average of the measured value of the reference gas before and behind measurement of sample gas, and the method B of asking for the absorbance of sample gas based on the measured value of the reference gas only before measurement of sample gas.
[0056] The result of having computed concentration by Approach A is shown in Table 1. The concentration obtained 2nd henceforth is standardized in Table 1, having used 1st measurement concentration as 1. The standard deviation of the computed concentration data was set to 0.0009 by Approach A.
[0057]
[Table 1]
方 法 A

1回目	2回目	3回目	4回目	5回目
1	1.0011	0.9996	0.9998	1.0011
6回目	7回目	8回目	9回目	10回目
0.9982	1	1.0014	1.0005	1.0006

[0058] The result of having computed concentration by Approach B is shown in Table 2. The concentration obtained 2nd henceforth is standardized even in Table 2, having used 1st measurement concentration as 1. The standard deviation of concentration data was set to 0.0013 by Approach B.
[0059]
[Table 2]

方 法 B

1回目	2回目	3回目	4回目	5回目
1	1.0024	1.0001	0.9996	1.0018
6回目	7回目	8回目	9回目	10回目
0.9986	1	1.0022	1.0014	1.0015

[0060] The average value of the quantity of light of the light obtained from the above thing by filling sample gas and the quantity of light of the light obtained by filling the reference gas before and behind that showed that concentration data with still less dispersion were obtained for the way of the approach of this invention of asking for an absorbance.
[0061]
[Effect of the Invention] Since the absorbance is calculated as mentioned above from the average of the quantity of light of the light obtained by filling measured gas, and the quantity of light of the light obtained by filling the reference gas before and behind that according to this invention according to claim 1 or 4, a part for the time variation before and behind measured gas determination can be amended by taking the average of the quantity of light of reference gas, and the effect of aging of system of measurement can be removed. Moreover, since the measurement result of the reference gas after measurement of measured gas also brings a measurement result of the reference gas before measurement of the following measured gas, it can utilize the measurement result of 1 time of reference gas for a duplex, and can raise effectiveness.
[0062] Moreover, since the absorbance is calculated from the average of the quantity of light of the light obtained by filling reference gas, and the quantity of light of the light obtained by filling the measured gas before and behind that according to this invention according to claim 2 or 5, a part for the time variation before and behind measured gas determination can be amended by taking the average of the quantity of light of measured gas, and the effect of aging of system of measurement can be removed.
[0063] Moreover, according to this invention according to claim 7, 8, or 9, it is CO2 about two kinds of measured gas. Since concentration can be made almost the same, it is 12CO2. A calibration curve and 13COs2 The range using a calibration curve can be narrowed. Since what has a good precision is obtained so that the range to be used is narrow, a calibration curve can raise the accuracy of measurement by limiting the range using a calibration curve.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the block diagram showing the whole isotope gas spectrometry equipment configuration.
[Drawing 2] It is the sectional view showing the structure of the cel room 11.
[Drawing 3] It is drawing showing the gas passageway when passing and washing pure reference gas in the gas passageway and cel room of isotope gas spectrometry equipment.
[Drawing 4] It is drawing showing the gas passageway when passing and washing pure reference gas in the gas passageway and cel room of isotope gas spectrometry equipment, and carrying out reference measurement.
[Drawing 5] It is drawing showing the condition in the middle of inhaling gase gas with the insufflation vessel 21 from an exhalation bag as reference gas does not flow 1st sample cel 11a and 2nd sample cel 11b.
[Drawing 6] After inhaling gase gas, **-SUGASU is mechanically extruded by whenever [- constant-speed] using the insufflation machine 21, and it is drawing showing the gas passageway when carrying out actinometry by each sensing element 25a and 25b in the meantime.
[Drawing 7] It is drawing showing the condition in the middle of inhaling sample gas with the insufflation vessel 21 from an exhalation bag as reference gas does not flow 1st sample cel 11a and 2nd sample cel 11b.
[Drawing 8] After inhaling sample gas, sample gas is mechanically extruded by whenever [- constant-speed] using the insufflation machine 21, and it is drawing showing the gas passageway when carrying out actinometry by each sensing element 25a and 25b in the meantime.
[Description of Notations]
D Infrared detection equipment
L Infrared light equipment
M1, M2 Flowmeter
N1, N2 Nozzle
V1 - V4 Bulb
11a The 1st sample cel
11b The 2nd sample cel
11c Reference cell
21 Insufflation Machine
24a The 1st wavelength filter
25a The 1st sensing element
24b The 2nd wavelength filter
25b The 2nd sensing element

[Translation done.]